

# Phonons in pristine and imperfect two-dimensional soft colloidal crystals

Ke Chen,<sup>1,2</sup> Tim Still,<sup>1</sup> Samuel Schoenholz,<sup>1</sup> Kevin B. Aptowicz,<sup>3</sup>  
Michael Schindler,<sup>4</sup> A. C. Maggs,<sup>4</sup> Andrea J. Liu,<sup>1</sup> and A. G. Yodh<sup>1</sup>

<sup>1</sup>*Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*

<sup>2</sup>*Beijing National Laboratory for Condensed Matter Physics and Key Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

<sup>3</sup>*Department of Physics, West Chester University, West Chester, Pennsylvania, 19383, USA*

<sup>4</sup>*Laboratoire PCT, Gulliver CNRS-ESPCI UMR 7083, 10 rue Vauquelin, 75231 Paris Cedex 05, France*

(Dated: January 10, 2013)

The vibrational modes of pristine and polycrystalline monolayer colloidal crystals composed of thermosensitive microgel particles are measured using video microscopy and covariance matrix analysis. At low frequencies, the Debye relation for two dimensional harmonic crystals is observed in both crystal types; at higher frequencies, van Hove singularities in the phonon density of states are significantly smeared out by experimental noise and measurement statistics. We introduce methods to correct for these errors, which can be applied to disordered systems as well as crystalline ones, and we show that error correction leads to considerably more pronounced van Hove singularities. Finally, quasi-localized low-frequency modes in polycrystalline two-dimensional colloidal crystals are identified and demonstrated to correlate with structural defects such as dislocations, suggesting that quasi-localized low-frequency phonon modes may be used to identify local regions vulnerable to rearrangements in crystalline as well as amorphous solids.

PACS numbers: 82.70.Dd, 61.72.-y, 63.20.kp

Recently, video microscopy has been cleverly employed to extract information about the dynamical matrix of ordered [1] and disordered [2] colloidal systems, using a covariance matrix analysis. This technical advance has opened a novel experimental link between thermal colloids and traditional atomic and molecular materials [3–12]. Along these lines, one ubiquitous feature of atomic glasses, the so-called “boson peak” due to an excess number of vibrational modes at low frequency [13, 14], has been observed in disordered colloidal packings [2, 4, 5]. Furthermore, connections have been established between “soft spots” associated with quasi-localized low-frequency vibrational modes and localized particle rearrangements in disordered colloids [8, 9, 15–17], reinforcing the possibility that such phenomena might exist in atomic and molecular glasses, as well.

The present paper has two primary themes. First, we use nearly perfect crystals to gain a better understanding of errors in the video-microscopy-covariance approach for studying phonon spectra, and to develop and demonstrate error correction approaches which are applicable even to disordered systems. Second, we study *imperfect* crystals in order to probe directly the effects of defects on phonon modes. We find that structural defects in the *imperfect* two-dimensional colloidal crystals are spatially correlated with quasi-localized low-frequency phonon modes. Thus, our experiments extend ideas about quasi-localized low-frequency modes and flow defects in colloidal glasses [8, 9, 17] to the realm of colloidal crystals and suggest that phonon properties can be used to identify crystal defects which participate in the material’s response to mechanical stress.

Specifically, we employ video microscopy and covari-

ance matrix analysis to explore the phonons of various two-dimensional soft colloidal crystals. By studying two-dimensional crystals [18], we avoid complications [19, 20] encountered by previous experiments which analyzed two-dimensional image slices within three-dimensional colloidal crystals to derive phonon properties [4, 10]. Our work is also complementary to earlier experiments by Keim, et al. [1] which studied two-dimensional crystals composed of particles interacting via magnetic-dipole forces and found good quantitative agreement between the dispersion relation measured by the covariance matrix technique and theoretical expectation. By contrast, the present experiments measure the vibrational density of states, which is much more susceptible to error, as well as the dispersion relations for crystals of particles with short-range interactions. In addition, we identify a narrow band of modes in imperfect crystals that is associated with crystal defects.

The experiments employed poly(*N*-isopropylacrylamide) or PNIPAM microgel particles, whose diameters decrease with increasing temperature. Particle diameters are measured to be 1.4  $\mu\text{m}$  at 24  $^{\circ}\text{C}$  by dynamic light scattering with a polydispersity of 5%. PNIPAM particles are loaded between two coverslips. Crystalline regions are formed as the suspension is sheared by capillary forces. The samples are then hermetically sealed using optical glue (Norland 65) and thermally cycled between 28  $^{\circ}\text{C}$  and room temperature for at least 24 hours to anneal away small defects. Particle softness permits the spheres to pack densely with stable contacts and yet still exhibit measurable thermal motions. Before data acquisition, samples equilibrate for 4 hours on the microscope stage. Bright-field microscopy images are ac-

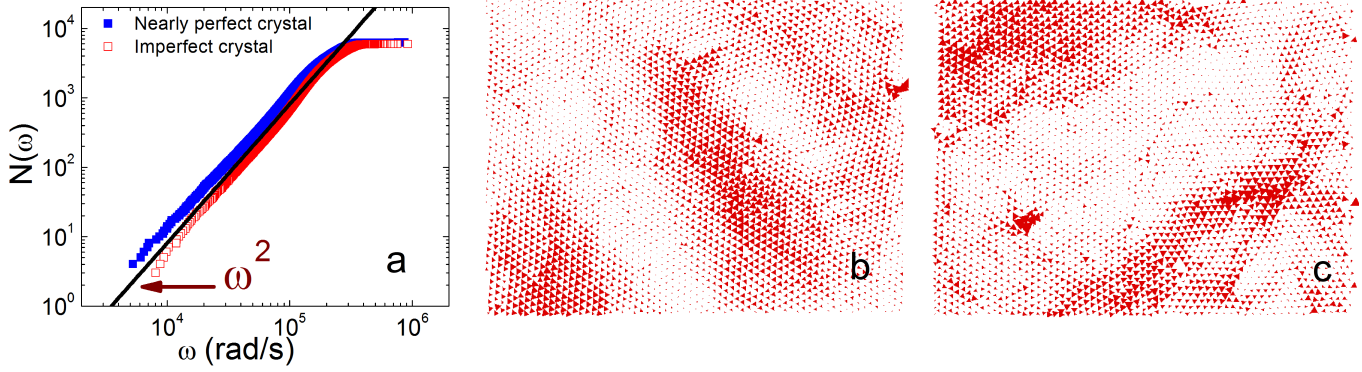


FIG. 1: (color online) Phonon modes in 2D colloidal crystals. a. Accumulated mode number,  $N(\omega)$ , as a function of frequency, for a nearly perfect crystal (blue squares) and an imperfect one (red square);  $\omega^2$  is drawn for comparison (black line). bc. Spatial distribution of a low-frequency mode for the (b) nearly perfect and (c) imperfect crystal; the direction and magnitude of polarization vectors are represented by the direction and size of the arrows.

quired at 60 frames per second with a total number of frames of 40,000. An image shutter speed of 1/4000 second is used. Each image contains about 3000 particles in the field of view. The trajectory of each particle in the video was then extracted using standard particle-tracking techniques [21]. Crystal quality is characterized by Fourier transformation of the microscopy images, and by spatial correlations of the bond orientational order parameter,  $\Psi_6$  [22]. To obtain intrinsic vibrational modes of the colloidal crystal samples, we employ covariance matrix analysis. Specifically, a displacement vector  $\mathbf{u}(t)$  that contains the displacement components of all particles from their equilibrium positions is extracted for each frame. A covariance matrix  $C$  is constructed with  $C_{ij} = \langle u_i u_j \rangle_t$ , where  $i$  and  $j$  run through all particles and coordination directions. To quadratic order, the stiffness matrix  $K$ , which contains the effective spring constants between particles, is proportional to the inverse of  $C$  with  $K = k_B T C^{-1}$ . Thus, by measuring the relative displacement of particles, interactions between particle pairs can be extracted and dynamical matrix constructed, i.e.,

$$D = \frac{K}{m} = \frac{(C^{-1})}{mk_B T}. \quad (1)$$

The dynamical matrix yields the eigenfrequencies and eigenvectors of the *shadow system*: the system of particles with the exact same interactions and geometry as the colloidal particles, but without damping. This approach of measuring phonons permits direct comparison to theoretical models, e.g., models that might be used to understand atomic and molecular crystalline solids.

The covariance matrix approach assumes harmonic potential energy landscape near the equilibrium configuration of the system. This assumption can be readily tested by the potential energy distribution of the obtained modes [22]. In our experiments, we find that some of the lowest frequency modes, typically less than 5 modes, do not satisfy the harmonic assumption, possibly

due to under-sampling of the lowest energy basins [23], or more likely due to small sample drifts. These non-harmonic modes are excluded from our analysis.

At low frequencies, Debye scaling requires that the phonon density of states  $D(\omega)$  scales with  $\omega^{d-1}$ , where  $d$  is the dimensionality of the system, or that  $N(\omega)$ , the number of modes below a certain frequency  $\omega$ , scales as  $\omega^d$  [24]. Debye scaling for two-dimensional crystals is clearly exhibited by both our perfect and imperfect monolayer colloidal crystals (see Fig. 1a). For more than one decade,  $N(\omega)$  follows a power law close to 2, as expected. The lowest frequency modes typically exhibit wave-like features as shown in Figs. 1b and c (more real space vector plots of low frequency modes can be found in supplementary material [22]). Thus we conclude that the Debye scaling observed in Fig. 1a is due to wave-like “sound modes.”

At higher frequencies, deviations from Debye behavior are observed in the phonon density of states,  $D(\omega)$ , as shown in Fig. 2a for the pristine crystal. For triangular two-dimensional crystals with harmonic interactions, the density of states has two van Hove singularities, one for longitudinal modes and one for transverse modes (solid lines in Fig. 2a); these singularities are expected to arise at the boundary of the first Brillouin zone. In contrast, Fig. 2a shows that the experimentally measured  $D(\omega)$  (black open circles) exhibits a smooth peak at an intermediate frequency and a shallow shoulder at higher frequency.

We identify the peak and shoulder as vestiges of van Hove singularities. Several factors may contribute to the rounding of van Hove singularities in a colloidal crystal. For example, particle polydispersity may break translational symmetry for the largest wave vectors, where van Hove singularities appear. The statistics associated with the finite number of frames (i.e., finite number of temporal measurements), as well as uncertainties in locating

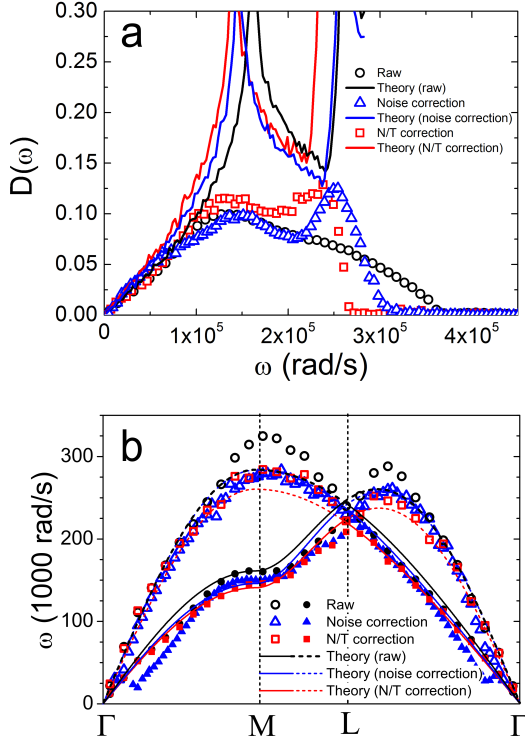


FIG. 2: (color online) a. Phonon density of states of two-dimensional colloidal crystals. DOS obtained from experimental data (black circles), DOS after suppressing non-nearest neighbor interactions in the stiffness matrix  $K$  (blue triangles), and DOS after N/T extrapolation (red squares). Numerically generated DOS for the harmonic triangular lattice (with matched sound speeds) is plotted as a guide of eye (solid lines). b. Dispersion curves for longitudinal (open symbols) and transverse modes (filled symbols) along high-symmetry directions, including uncorrected experimental data (black circles), data after non-nearest neighbor noise suppression (blue triangles), data after N/T extrapolation (red squares). Theoretical expectations are plotted in dashed (longitudinal) and solid (transverse) lines with matched colors

particle positions, can introduce noise into the covariance matrix and thus into its eigenvalues and eigenvectors. In the following, we discuss these effects, and we show how to recover some of the expected behavior by applying corrections to the experimental data.

One cause of the reduced or diminished peaks in the DOS is noise that gives rise to apparent interactions between non-nearest neighbor particles in the stiffness matrix. In experiment, the effective spring constants between non-nearest neighbor particles are never zero; instead they take on small values fluctuating around zero. These apparent interactions between distant particles are unlikely to be physical, since PNIPAM particles interact through direct soft sphere contacts. To examine the effects of the spurious random interactions between distant particles, we set the matrix elements between non-nearest

neighbor particles in the stiffness matrix  $K$  to be zero with corresponding corrections to the diagonal terms as required by translational symmetry, and then we solve for new eigenvalues. The blue triangles in Fig. 2a show that suppression of the effects of these spurious interactions in the dynamical matrix leads to recovery of peaks at the frequencies expected for van Hove singularities, while maintaining Debye scaling at low frequencies.

The apparent interactions between non-nearest neighbor particles are likely caused by a combination of two sources of error: uncertainty in particle displacement determination and limited statistics [25]. We note that in the limit of perfect statistics (i.e., where the covariance matrix is calculated from an infinite number of time frames), measurement error modifies the effective interactions in a way that is mathematically similar to the effect of quantum fluctuations at high temperature, as described by Wigner-Kirkwood theory, and to integration errors in molecular dynamics simulations [22]. Thus, in the absence of statistical error, measurement error would give rise to further neighbor interactions but would not smooth out the van Hove singularities.

We now consider the opposite case, where there is no measurement error but there is error associated with the quality of statistics used to calculate the covariance matrix. A key quantity is  $R = N/T$ , where  $N$  is the number of degrees of freedom and  $T$  is the number of independent time frames used. Random matrix theory suggests that the eigenvalue distribution should converge to its limiting  $R = 0$  values linearly with  $R$  [26]. We have shown that the eigenvalues also converge linearly for crystals [22]. In the absence of measurement error, one could then expect to obtain van Hove singularities in the density of states by extrapolating to the limiting  $R = 0$  frequencies. The comparison between the raw data (black circles) and extrapolated data (red squares) in Fig. 2a shows that the corrections are larger at higher frequencies, as expected, and that extrapolation modifies the shoulder at the second van Hove singularity into a small peak.

We also studied the effect of errors on the dispersion relation, which is obtained from the eigenmodes of the covariance matrix. For each eigenmode, spectral functions for longitudinal and transverse components are calculated for high-symmetry directions [27, 28], and the wave vector corresponding to the maximum of the spectral function,  $k_{max}(\omega)$  is extracted. The binned dispersion curves (black symbols in Fig. 2b) largely follow the theoretical expectation, obtained by fitting to the low frequency part of the curve to obtain the longitudinal and transverse speeds of sound, as shown in Fig. 2b. However, the measured dispersion relation has a stronger dependence on  $k$ , especially for the longitudinal branch. When we suppressed further neighbor interactions, the resulting dispersion relation (blue symbols in Fig. 2b) agrees significantly better with the theoretical expectation. We also extrapolated to the limit of perfect statistics, where

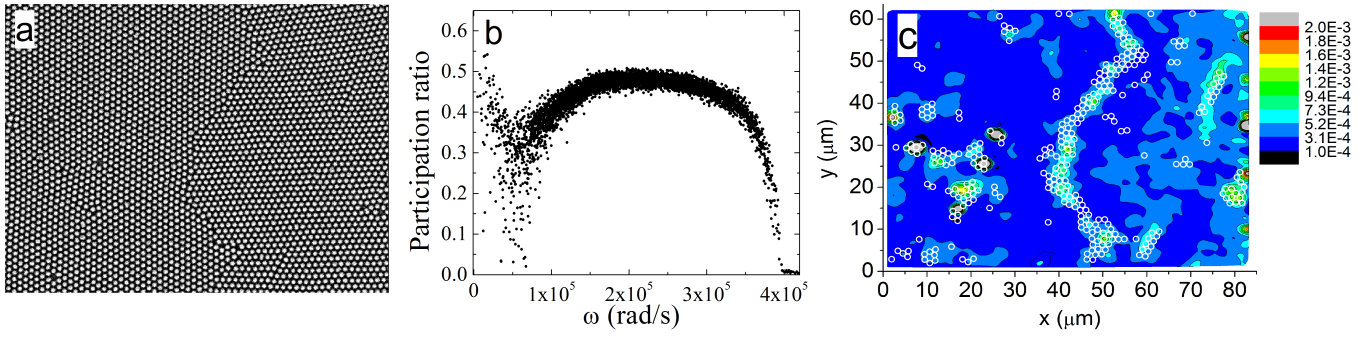


FIG. 3: (color online) Low frequency modes in a colloidal crystal with defects. a. A snapshot of an imperfect PNIPAM crystal with a grain boundary in the middle of the field of view. b. Participation ratio for eigenmodes in crystal with defects. c. Color contour plots indicate polarization magnitudes for each particle, summed over the low frequency modes with participation ratio less than 0.2. Circles indicate "defect" particles identified by local structural parameters.

$R = N/T$  approaches zero. We find from simulations that, like the mode frequencies, the dispersion relation approaches its limiting  $R = 0$  value linearly in  $R$ . Extrapolation of the data (red symbols in Fig. 2b) also leads to excellent agreement with theory. Thus, *the dispersion relation appears far less sensitive than the density of vibrational states to both of the leading sources of error in the covariance matrix technique: measurement error in the positions of particles and limited statistics.*

From the data corrected by suppressing further neighbor interactions and by extrapolating  $R$  to zero, we obtain (2D) bulk moduli of  $2.2 \cdot 10^{-5}$  kg/s<sup>2</sup> and  $1.8 \cdot 10^{-5}$  kg/s<sup>2</sup>, and shear moduli of  $6.0 \cdot 10^{-6}$  kg/s<sup>2</sup> and  $5.6 \cdot 10^{-6}$  kg/s<sup>2</sup>, respectively. The measured shear modulus is in line with (3D) bulk rheology measurements of PNIPAM suspensions [29].

Finally, we explored phonons in the imperfect two-dimensional colloidal crystal shown in Fig. 3a. Most of the low frequency modes are extended and wave-like (as in Fig. 1c), consistent with the observation of Debye scaling in the accumulated number of modes,  $N(\omega)$ , shown in Fig. 1a. To take a closer look, we calculated the participation ratio,  $p(\omega)$ , which measures the degree of spatial localization of a mode  $\omega$  is defined as  $p(\omega) = (\sum_i m_i |\mathbf{e}_{\omega,i}|^2)^2 / (N \sum_i m_i^2 |\mathbf{e}_{\omega,i}|^4)$ , where  $\mathbf{e}_{\omega,i}$  is the polarization vector in mode  $\omega$  and  $m_i$  is the mass, of particle  $i$ . Fig. 3b shows that while most of the modes have participation ratios near 0.5, the value expected for a plane wave, a few of the low-frequency modes have a significantly smaller participation ratio.

The low-participation-ratio low-frequency modes observed in Fig. 3b are reminiscent of quasi-localized low-frequency modes observed in colloidal glasses [5, 8]. In jammed packings, such modes have unusually low barriers to rearrangements [16] and have been used to identify a population of soft spots that serve as flow defects when the packings are sheared [17]. Experiments on the PNIPAM colloidal glass similarly found that rearrangements induced by shrinking all the particles occur at soft

spots [8]. In crystalline systems, it is known that rearrangements tend to occur at crystal defects, particularly dislocations. Our observation of quasi-localized modes in imperfect crystals therefore raises the question of whether the modes are spatially concentrated near structural defects such as dislocations.

In the colored contour map in Fig. 3c, we plot the spatial distribution of the quasi-localized low-frequency modes with a participation ratio less than 0.2, i.e.,  $\frac{1}{N_{0.2}} \sum_{pr(\omega) < 0.2} (\tilde{\mathbf{e}}_i^\omega)^2$ , where  $N_{0.2}$  is the number of modes with participation ratio below 0.2,  $i$  is the particle number, and  $\tilde{\mathbf{e}}_i^\omega$  is the polarization vector of particle  $i$  in mode  $\omega$ . The white circles in Fig. 3 indicate structural defects in the crystal sample, identified by local structural parameters. Here a particle is identified as a "defect" particle when the number of its nearest neighbors is not 6, or the magnitude of the local bond orientational order parameter  $\Psi_6 = \frac{1}{N_{nn}} \sum_k^{N_{nn}} e^{6i\theta_{jk}}$  is less than 0.95.

The spatial correlation between quasi-localized low-frequency modes (soft modes in crystals) and structural defects in colloidal crystals is obvious in Fig. 3c. In particular, such modes in crystals appear to single out structural defects susceptible to external perturbations such as dislocations or interstitials; we note that they are less effective at picking out vacancies, which are mechanically more stable. The correlation between quasi-localized modes and structural defects is robust to variation of the participation ratio cutoff between 0.1 and 0.3 [22].

The observation that quasi localized modes are concentrated in regions prone to rearrangements not only in disordered solids [8, 17], but also in crystalline ones, suggests that such modes may be a general identifier of flow defects. Indeed, these modes, together with those in the boson peak at somewhat higher frequencies [30], could serve as a useful link for understanding systems spanning the entire gamut from the perfect crystal to the most highly disordered glass.

We thank T.C. Lubensky, V. Markel, J. Mattson, G. Mele, P. Yunker, and M. Gratale for helpful discussions. This work was funded by DMR12-05463, PENN-MRSEC DMR11-20901, NASA NNX08AO0G, DMR-1206231 (K.B.A.), T.S. acknowledges support from DAAD.

- 
- [1] P. Keim, G. Maret, U. Herz, H. H. von Grünberg, Phys. Rev. Lett. **92**, 215504 (2004).
  - [2] A. Ghosh, V. K. Chikkadi, P. Schall, J. Kurchan, and D. Bonn, Phys. Rev. Lett. **104**, 248305 (2010).
  - [3] J. Baumgartl, M. Zvyagolskaya, and C. Bechinger, Phys. Rev. Lett. **99**, 205503 (2007).
  - [4] D. Kaya *et al.*, Science **329**, 656. (2010).
  - [5] K. Chen *et al.*, Phys. Rev. Lett. **105**, 025501 (2010).
  - [6] N. L. Green, D. Kaya, C. E. Maloney and M. F. Islam, Phys. Rev. E **83**, 051404 (2011).
  - [7] P. J. Yunker, K. Chen, Z. Zhang, and A. G. Yodh, Phys. Rev. Lett. **106**, 225503 (2011).
  - [8] K. Chen, *et al.*, Phys. Rev. Lett. **107**, 108301 (2011).
  - [9] A. Ghosh, V. Chikkadi, P. Schall, and D. Bonn, Phys. Rev. Lett. **107**, 188303 (2011).
  - [10] A. Ghosh, R. Mari, V. Chikkadi, P. Schall, A. C. Maggs, D. Bonn, Physica A **139**, 3061 (2011).
  - [11] P. J. Yunker, K. Chen, Z. Zhang, W. G. Ellenbroek, A. J. Liu, and A. G. Yodh, Phys. Rev. E **83**, 011403 (2011).
  - [12] P. Tan, N. Xu, A. B. Schofield, and L. Xu, Phys. Rev. Lett. **108**, 095501 (2012).
  - [13] W. A. Phillips (editor), *Amorphous Solids* (Springer-Verlag, 1981).
  - [14] R. O. Pohl, X. Liu, and E. Thompson, Rev. Mod. Phys. **74**, 991 (2002).
  - [15] A. Widmer-Cooper, H. Perry, P. Harrowell, and D. R. Reichman, Nature Physics **4** 711 (2008).
  - [16] N. Xu, V. Vitelli, A. J. Liu, and S. R. Nagel, Eur. Phys. Lett. **90**, 56001 (2010).
  - [17] L. Manning, A. J. Liu, Phys. Rev. Lett. **107**, 108302 (2011).
  - [18] F. M. Peeters, X. Wu, Phys. Rev. A **35**, 3109 (1987).
  - [19] M. Schindler, A. C. Maggs, Soft Matter **8**, 3864 (2012).
  - [20] C. A. Lemarchand, A. C. Maggs, and M. Schindler, Eur. Phys. Lett. **97** 48007 (2012) , Eur. Phys. Lett. **99** (2012) 49904 (erratum).
  - [21] J. C. Crocker, D. G. Grier, J. Colloid. Interf. Sci. **179**, 298 (1996).
  - [22] See EPAPS Document No. XXX for a discussion of additional experimental details. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
  - [23] B. Hess, Phys. Rev. E **62**, 8438 (2000).
  - [24] N. W. Aschcroft and N. D. Mermin, *Solid State Physics*, (Holt, Rinehart, and Winston, New York, 1976).
  - [25] S. Henkes, C. Brito, and O. Dauchot, Soft Matter, **8**, 6092 (2011).
  - [26] Z. Burda, A. Gorlich, A. Jarosz, and J. Jurkiewicz, Physica A **343** 295 (2004).
  - [27] L. Silbert, A. J. Liu, and S. Nagel, Phys. Rev. E **79**, 021308 (2009).
  - [28] V. Vitelli, N. Xu, M. Wyart, and A. J. Liu, Phys. Rev. E **81**, 021301 (2010).
  - [29] H. Senff and W. Richtering, J. Chem. Phys. **111**, 1705 (1999).
  - [30] A. Chumakov, *et al.*, Phys. Rev. Lett. **106**, 225501 (2011).